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CYCLIC VOLTAMMETRIC INVESTIGATION OF DISILENES(U)

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WISCONSIN UNIV-MADISON DEPT OF CHEMISTRY

R. D. SHEPHERD ET AL. 1988 AFOSR-TR-88-0383

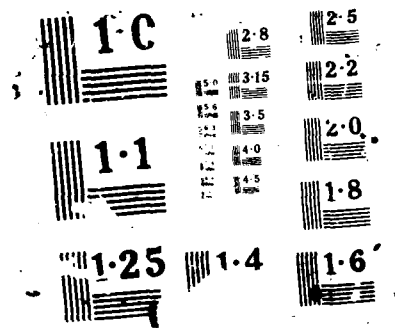
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Cyclic Voltammetric Investigation of Disilenes

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Three tetraaryldisilenes and two dialkyldiaryldisilenes were investigated by cyclic voltammetry, all undergoing irreversible oxidation and reduction. The oxidation potentials were similar for all five compounds, but the reduction potentials were lower for the tetraaryldisilenes than for the dialkyldiaryldisilenes.

The electronic properties of disilenes are not well understood. Their photoelectron spectra have not been reported and uv-visible spectroscopy provides only limited information.¹⁾ Silicon-29 shielding anisotropy measurements have provided some knowledge of the electronic structure of the silicon-silicon double bond,²⁾ and Weidenbruch and coworkers have reported ESR spectra assigned to disilene anion-radicals obtained indirectly.³⁻⁵⁾ We have used cyclic voltammetry (CV) as an experimental method to gain further insight into the molecular orbital patterns of disilenes.

The isolable disilenes investigated were prepared by dimerization of the silylene generated from photolysis of the corresponding trisilane.^{6,7)} They are listed in Table 1 with their oxidation and reduction peak potentials. A typical voltammogram is shown in Fig. 1; all the disilenes exhibited similarly shaped waves.⁸⁾

The disilenes 1-5 undergo irreversible oxidation and reduction in tetrahydrofuran at room temperature.⁹⁾ The oxidation potentials for all five compounds are similar (Table 1), indicating that the highest occupied molecular orbital (HOMO) of each species lies at approximately the same energy level. The reduction potentials, however, depend on the substitution pattern. The tetraaryldisilenes 1-3 are reduced at -2.0 to -2.2 V, whereas the dialkyldiaryl derivatives 4 and 5 undergo reduction at about -2.6 V (Table 1). These results indicate that the lowest unoccupied molecular orbital (LUMO) of tetraaryldisilenes is lower in energy than the LUMO of dialkyldiaryldisilenes.

In the solid state structure of both dialkyldiaryldisilenes 4⁶⁾ and 5,¹²⁾ the mesityl rings are essentially orthogonal to the silicon-silicon double bond. This conformation allows little pi-conjugation between the aromatic substituents and the double bond. In the solid state structure of the tetraaryl derivative 1,

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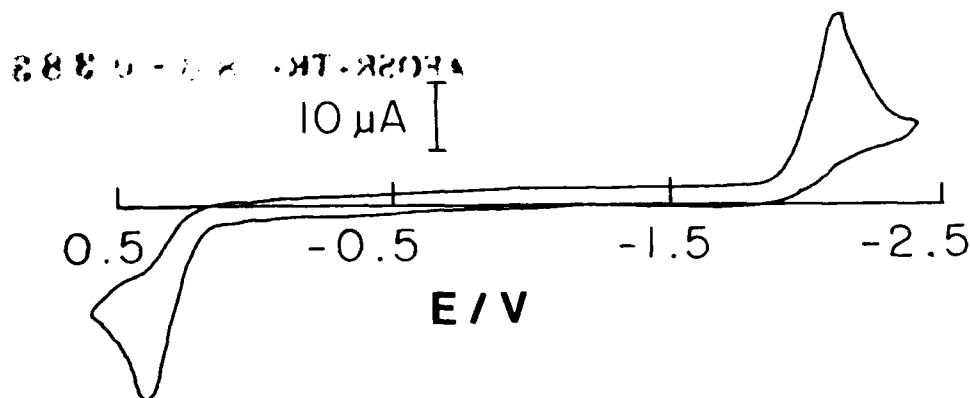


Fig. 1. Cyclic voltammogram for disilene 1.

Table 1. Peak Potentials of Disilenes from Cyclic Voltammetry^{a)}

$$\begin{array}{c}
 R^1 \quad R^2 \\
 \diagdown \quad \diagup \\
 Si=Si \\
 \diagup \quad \diagdown \\
 R^2 \quad R^1
 \end{array}$$

Disilene	R ¹	R ²	Ep.Ox.(V)	Ep.Red.(V)
1	Mes ^{b)}	Mes ^{b)}	+0.38	-2.12
2	Xyl ^{c)}	Xyl ^{c)}	+0.47	-2.03
3	Tbp ^{d)}	Tbp ^{d)}	+0.48	-2.20
4	Mes ^{b)}	t-Bu	+0.54	-2.66
5	Mes ^{b)}	Ad ^{e)}	+0.36	-2.64

a) Potentials are the average of two or three scans acquired on different days and were measured versus SCE at room temperature in THF containing 0.1 M [NBu₄]⁺[PF₆]⁻ at a platinum disk electrode (0.28 cm²) with a scan rate of 200 mV/s. The ferrocene/ferrocinium ion couple was measured at +0.61V in this system.

b) Mes = 2,4,6-trimethylphenyl.

c) Xyl = 2,4-dimethylphenyl.

d) Tbp = 4-*tert*-butyl-2,6-dimethylphenyl.

e) Ad = 1-adamantyl.

however, two of the aromatic rings are nearly coplanar with the double bond so π -conjugation is possible.⁶⁾ With the assumption that the major conformer in solution is similar to that observed in the solid state, we offer the MO diagrams shown in Fig. 2 as a description of orbital organization in disilenes. In the dialkyldiaryldisilenes, orbital mixing between disilene π or π^* orbitals and those

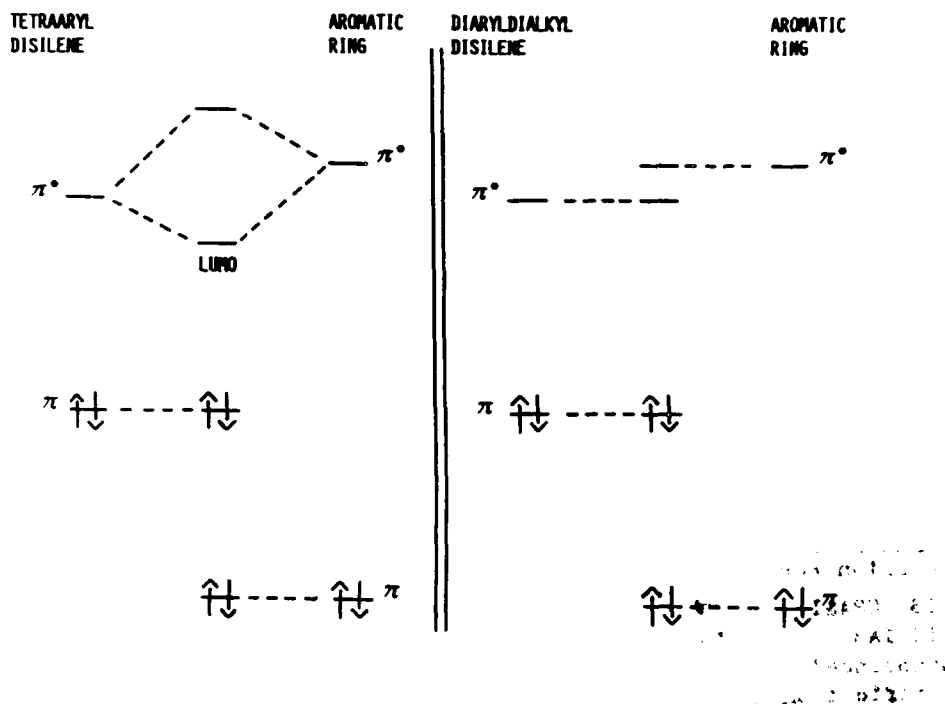


Fig. 2. MO diagrams for aryl-substituted disilenes.

of the aromatic rings is precluded by the orthogonality of the π -systems. In the tetraaryldisilenes, interaction between the filled disilene and ring π orbitals is also slight, presumably because the energy difference between these orbitals is large. However, significant mixing of the disilene and aromatic ring π^* orbitals does occur in the tetraaryldisilenes, lowering the energy of the resulting LUMO.

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- 8) CV measurements were acquired on a BAS Electrochemical Analyzer equipped with a PAR electrochemical cell which was operated inside a drybox under nitrogen.
- 9) For comparison, tetraphenylethylene undergoes reversible reduction at -2.47 V (in THF vs. Ag wire)¹⁰⁾ and oxidation at +1.33 V (in TFA/CH₂Cl₂ vs. SCE).¹¹⁾
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